Densities and bubble points of binary mixtures of carbon dioxide and *n*-heptane and ternary mixtures of *n*-butane, *n*-heptane and *n*-hexadecane[1]

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Abstract

The densities of three mixtures of carbon dioxide and *n*-heptane and three mixtures of *n*-butane, *n*-heptane and *n*-hexadecane were measured. The binary mixtures were studied over the temperature range 302 to 459 K and the pressure range 3.61 to 55.48 MPa at the following carbon dioxide mole fractions: 0.2918, 0.3888 and 0.4270. The ternary mixtures were studied over the temperature range 405 to 469 K and the pressure range 0.7 to 24 MPa at the following *n*-butane mole fractions: 0.1161, 0.1967 and 0.2314 and corresponding *n*-heptane mole fractions: 0.7151, 0.6499 and 0.6218. The measurements were carried out in an automated isochoric instrument and their accuracy is estimated to be better than ± 0.1 per cent. The bubble points of the mixtures were also determined from an analysis of the experimental isochores in the one- and two-phase regions. The new measurements have been used to assess the performance of the Peng-Robinson equation of state and the one-fluid corresponding states model. In single phase regions the performance of the one-fluid model is found to be superior to that of the Peng-Robinson equation. The latter performs well for bubble points provided that optimised interaction parameters are used. As an interpolation tool, the one fluid model is found to reproduce the ternary mixtures within the experimental uncertainty.

Keywords: Density; Bubble points; Experimental method; Model; Binary mixtures; Ternary mixtures.

1. **Introduction**

Hydrocarbons form the major components of oil and natural gas. Their optimal recovery from natural deposits as well as their subsequent processing rely to a considerable extent upon good knowledge of their thermodynamic properties and, in particular, of their phase behaviour. Cubic equations of state are widely used for this purpose and their position remains unchallenged at present in reservoir simulation. Indeed, their computational simplicity and the existence of an analytical solution for the density at specified temperature and pressure make these models attractive for numerous applications. However, many petroleum reservoirs being developed today are much deeper than has been the case hitherto with the consequence that higher temperatures (up to 473 K) and pressures (up to 120 MPa) need to be considered and the thermodynamic models properly validated in these regions.

The experimental work presented here is part of a programme of accurate measurements of the phase behaviour and density of two-, three- and four-component fluid mixtures of precisely known composition. Density measurements are made on the bubble curve and in the compressed liquid and supercritical fluid regions at pressures up to 60 MPa and temperatures up to 473 K. The bubble points are determined from an analysis of the experimental isochores [1,2]. Synthetic mixtures rather than natural petroleum fluids are chosen because the mole fraction of each component can be accurately known. This leaves the matter of how best to characterise a natural fluid as a separate, albeit important, problem.

The objective of the present work is two-fold: first to generate accurate data in difficult experimental regions and second to assess the performance of two thermodynamic models in the high-temperature high-pressure regime by comparison with the new experimental results. The present paper is concerned with binary mixtures of carbon dioxide and *n*-heptane and ternary mixtures of *n*-butane, *n*-heptane and *n*-hexadecane. To our knowledge, there are no available measurements in the literature on

these systems. The evaluation of the performance of the selected Peng-Robinson and one-fluid corresponding states models relies therefore solely on the present results.

2. Experimental

The measurements reported here were carried out in an isochoric instrument described previously [1,2]. The *n*-butane used in the experiments was supplied by Linde Gas UK and had a mole fraction purity of 0.9995. Carbon dioxide was supplied by BOC Ltd and had a mole fraction purity of 0.99995. *n*-Heptane and *n*-hexadecane were supplied by Aldrich and had mole fraction purities of 0.99. The mass of each substance introduced into the pressure vessel was determined gravimetrically. The vessel was initially evacuated. The components that are liquid under ambient conditions (*n*-heptane, *n*-hexadecane) were injected by means of syringes while the compressed gases or liquids (carbon dioxide, *n*-butane) were injected from sample cylinders which were weighed with a precision of ±1 mg before and after each injection.

The temperature was measured by means of a platinum resistance thermometer embedded in a close-fitting aluminium jacket that surrounded the pressure vessel. The thermometer was calibrated by comparison with a transfer-standard platinum resistance thermometer which had itself been calibrated by the UK National Physical Laboratory on ITS-90. It is estimated that the uncertainty of the temperature measurements is ±0.01 K. The pressure was measured with a transducer (Paroscientific Model 410KR-HT-101) located in a separate thermostat maintained at 313.15 K. This transducer was calibrated in *situ* over the range 1 to 50 MPa against a Desgranges et Huot pressure balance having a stated uncertainty of ±0.004 percent. It is estimated that the maximum overall uncertainty of the pressures measured during the course of the experiment did not exceed the greater of ±0.02 percent and 5 kPa. The experimental procedure can be found elsewhere [2].

2.1. Experimental bubble-points and densities

Three mixtures of *n*-heptane and carbon dioxide were investigated over the temperature range 302 to 459 K and the pressure range 3.61 to 55.48 MPa at the following carbon dioxide mole fractions: 0.2918, 0.3888 and 0.4270. The experimental compressed liquid and supercritical densities as well as the bubble points for this system are presented in table 1 and the full measurements spanning both the two-phase and single phase regions are depicted in figure 1.

Three mixtures of *n*-butane, *n*-heptane and *n*-hexadecane were investigated over the temperature range 405 to 469 K and the pressure range 0.7 to 24 MPa at *n*-butane mole fractions of 0.1161, 0.1967 and 0.2314 and corresponding *n*-heptane mole fractions of 0.7151, 0.6499 and 0.6218. The experimental compressed liquid and supercritical densities as well as the bubble points for this system are presented in table 2 and the full measurements spanning both the two-phase and single phase regions are depicted in figure 2.

The break points in the isochores, which correspond to bubble-point conditions, can be clearly seen in figures 1 and 2 which include all the data taken on both systems. The determined bubble point pressures and temperatures of the mixtures as well as the corresponding saturated liquid densities are presented in tables 1 and 2 as values with the superscript s along with the single-phase densities. The data collected in the two-phase region have been omitted in these tables. On the basis of uncertainties in the measured quantities discussed above, we estimate that the overall uncertainty in density at specified temperature, pressure and composition is less than ±0.1 percent. The overall uncertainty of the bubble pressure at a specified composition is also estimated to be less than ±0.1 percent.

3. Thermodynamic models

Two models were chosen to represent the experimental data reported in this work: the industry-standard Peng-Robinson equation and the more advanced one-fluid corresponding-states model.

3. 1. The Peng-Robinson equation of state

The Peng-Robinson equation of state [3] is given by:

$$p = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2}, \tag{1}$$

where p is the pressure, T is the temperature, R is the gas constant, V is the molar volume and a and b are parameters obtained for a pure component from the critical temperature, critical pressure and the acentric factor. For a mixture of N components, a and b are generally given by the following mixing rules:

$$a = \sum_i^N \sum_j^N x_i x_j a_{ij}, \tag{2}$$

$$b = \sum_i^N \sum_j^N x_i x_j b_{ij}. \tag{3}$$

The cross term parameters a_{ij} and b_{ij} are given by the following combining rules

$$a_{ij} = (1-k_{ij})(a_{ii}a_{jj})^{1/2}, \tag{4}$$

$$b_{ij} = 0.5(b_{ii} + b_{jj})(1-l_{ij}), \tag{5}$$

where k_{ij} and l_{ij} are binary interaction parameters.

Cubic equations of state such as the Peng-Robinson model are known for their poor predictions of liquid density. Peneloux *et al*. [4] proposed a method, known as volume translation or correction, which goes someway towards remedying this deficiency. The molar volume V in equation (1) is replaced by (V + t), where t is the volume translation and V is the corrected molar volume. For a pure substance, t may be

adjusted such that the predicted molar volume of the saturated liquid is in agreement with experimental data at one temperature. Alternatively, a temperature dependent correlation may be adopted and fitted to experimental density data along the entire saturated liquid line. In this work, the correction proposed by Magoulas and Tassios [5] has been employed:

$$t = t_0 + (t_c - t_0)\exp\left(\lambda\,|1 - T_r\,|\right). \tag{6}$$

Here, t_c and λ are specified as functions of the critical constants and the acentric factor, $T_r = T/T_c$ and T_c is the critical temperature. A key property of the volume correction is that it has no effect on the calculated phase boundaries provided that, in a mixture, t is given by

$$t = \sum_{i=1}^{N} x_i t_i \,, \tag{7}$$

where t_i is the translation for component i.

3.2. The one-fluid model

In this model, a mixture is considered as an hypothetical pure substance while the reference fluid is chosen to be a real pure component, preferably similar in structure to the components of the mixture [6, 7]. Thus, the residual part of the Helmholtz energy of the mixture is written as

$$A^{\mathrm{res}}(V,T,x) = f_x A_0^{\mathrm{res}}(V/h_x, T/f_x)\,, \tag{8}$$

where the scaling parameters h_x for the molar volume and f_x for the temperature are dependent on the distance and energy scaling parameters for all binary interactions in the mixture including those for like (h_{ii}, f_{ii}) and unlike (h_{ij}, f_{ij}) interactions. Here, A_0^{res} is the residual Helmholtz energy of the reference substance. Any thermodynamic property of the mixture can be derived from the Helmholtz energy by standard manipulations.

The scaling parameters for like interactions are obtained from the properties of the pure substances whereas those for unlike ones are obtained from the following mixing rules

$$h_x = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j h_{ij}\,, \tag{9}$$

$$h_x f_x = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j f_{ij} h_{ij}\,. \tag{10}$$

The parameters h_{ii} and f_{ii} of the pure substance i are given by

$$h_{ii} = (V_i^{\mathrm{c}} / V_0^{\mathrm{c}})\varphi_{i,0}(V_i^{\mathrm{R}}, T_i^{\mathrm{R}})\,, \tag{11}$$

$$f_{ii} = (T_i^{\mathrm{c}} / T_0^{\mathrm{c}})\theta_{i,0}(V_i^{\mathrm{R}}, T_i^{\mathrm{R}})\,. \tag{12}$$

where $\theta_{i,0}$ and $\varphi_{i,0}$ are shape factors of substance i with reference to a structurally dissimilar substance indicated by the subscript 0. Here, the superscript c indicates a value at the critical point and superscript R a reduced property. The unlike scaling parameters are generally obtained from the Lorentz-Berthelot combining rules

$$f_{ij} = \xi_{ij}(f_{ii} f_{jj})^{1/2}\,, \tag{13}$$

$$h_{ij} = \eta_{ij}\{(h_{ii}^3 + h_{jj}^3)/2\}^3\,. \tag{14}$$

in which ξ_{ij} and η_{ij} are temperature-independent binary interaction parameters. The size parameter η_{ij} is sensitive to size effects according to the average potential model which constitutes the underlying foundation of the one-fluid approach. Evidence from comparison with virial coefficient fits points to a value of less than unity for the energy parameter ξ_{ij} [8]. It is not certain however that this applies to the liquid phase.

4. Results and discussion

As shown elsewhere [9], the Peng-Robinson model represents relatively better the phase behaviour properties than the single phase properties or the saturated densities. In view of this finding, the binary interaction parameters of the Peng-Robinson equation were determined from fits to the bubble-point pressures. The one-fluid model was

however found to represent better the single phase properties and the binary interaction parameters of the mixtures were therefore determined from the liquid and supercritical densities obtained in this work using a non-linear algorithm based on the method of Powell [10].

The optimal parameters of the Peng-Robinson model were found to be: α_{12} = 0.1223 and $\beta_{12} = 0$ for the carbon dioxide and *n*-heptane system. When these values were used, the deviations of the calculated bubble point pressures of the binary mixtures from the experimental values of tables 1 were less than 1.5 per cent. The results of the unoptimised model with $\alpha_{12} = 0$ were however found to be inaccurate and deviated by up to 38 per cent. The deviations of the saturated liquid, compressed liquid and supercritical densities are illustrated in figure 3. In general, the deviations are less than 5 per cent except for the saturated densities. One can also see in the figure the effect of volume translation on the saturated liquid densities. There is a significant improvement in the performance of the model when volume translation is included. The saturated data are now represented within less than 3 per cent. The translation technique was extended only some distance from the saturation curve since as found previously [9] its performance starts to deteriorate as evidenced by the trends in the values of figure 3.

The deviations of the Peng-Robinson model from the experimental data for the ternary system are shown in figure 4 for the unoptimised case only. As the interaction parameters of the constituent binary pairs are not all available, optimisation has not been attempted. The bubble points of table 2 were found to deviate by up to 16 percent when the unoptimised model was employed..

The reference substance used in the one-fluid model was carbon dioxide for which the equation of state of Span and Wagner [11] was employed. The two binary parameters of this model were fitted to the single phase density data and the resulting values are ξ_{12} = 1.316 and η_{12} = 1.225 for carbon dioxide plus *n*-heptane. The deviations of the model are within ± 0.6 per cent as shown by figure 5. For ternary mixtures interaction parameters for each binary pair are required. These interaction parameters are

however unavailable. Nevertheless for interpolation purposes, the experimental data were fitted to the one-fluid model in order to determine values for the six interaction parameters. It must be pointed out that the parameters determined in this way are not the same as the ones determined in the normal way, i.e. by fitting the binary data separately. The resulting values, namely $\xi_{12} = 0.9309$, $\eta_{13} = 1.430$, $\xi_{23} = 0.9609$, $\eta_{12} = 0.9609$, $\xi_{13} = 0.4999$ and $\eta_{23} = 1.083$ where the subscripts 1, 2 and 3 refer to *n*-butane, *n*-heptane and *n*-hexadecane, respectively are not unreasonable. The resulting deviations of the model are shown in figure 6 and are within the experimental uncertainty. This finding serves to emphasise the importance of experimental data in improving the performance of thermodynamic models. The predictions with all binary parameters set equal to unity of the one-fluid model for the ternary mixtures are shown in figure 4 and are found to deviate by up to 3 per cent. The deviations are brought within the experimental uncertainty when optimised parameters are used as shown by figure 6.

5. Conclusion

New measurements of the phase behaviour and density of three binary mixtures of carbon dioxide and *n*-heptane and three ternary mixtures of *n*-butane, *n*-heptane and *n*-hexadecane have been made which cover a wide range of temperatures and pressures. The results have been used to obtain optimised binary parameters for the Peng-Robinson and one-fluid models. The optimised Peng-Robinson model was found to represent the bubble pressures to within ± 1.5 per cent for the binary mixtures. The densities predicted by the model are however not accurate. The inclusion of a volume correction improved the predictions of the liquid densities on or near the saturation curve. The one-fluid model, yields accurate results for the single phase properties. It is found to be a remarkable interpolating tool for the ternary mixtures. Work is currently under way to extend the model to deal accurately with phase boundaries. On the experimental level

work is also planned to study the binary constituents of the ternary system reported in this paper.

LIST OF SYMBOLS

A	molar Helmholtz free energy
a	parameter in Peng-Robinson equation
b	parameter in Peng-Robinson equation
f	temperature scaling parameter
h	volume scaling parameter
k	binary interaction parameter
l	binary interaction parameter
p	pressure
R	universal gas constant
t	molar volume translation
T	temperature
V	molar volume
x	mole fraction

Greek letter

α	coefficient in correlation of binary parameter
β	coefficient in correlation of binary parameter
φ	shape factor
θ	shape factor
η	binary interaction parameter
ξ	binary interaction paremeter
ρ	amount-of-substance density

Subscript

c	critical
calc	calculated
exp	experimental
i,*j*	component indices
r	reduced

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Table 1. Pressure p, amount-of-substance density ρ and temperature T of $\{x_1CO_2 + (1-x_1)C_7H_{16}\}$. Superscript s indicates a saturated condition (bubble point).

T/K	p/MPa	ρ/mol·m^{-3}	T/K	p/MPa	ρ/ mol·m^{-}	T/K	p/MPa	ρ/mol·m^{-3}
	x_1=0.2918			x_1=0.3888			x_1=0.4270	
362.90^s	4.378^s	7535.4^s	321.08^s	4.040^s	8748.5^s	301.76^s	3.461^s	9340.9^s
363.22	4.538	7535.3	322.29	4.812	8747.9	316.28	13.956	9333.5
376.71	10.989	7529.8	331.39	10.548	8743.6	322.33	18.288	9330.4
390.65	17.706	7524.1	358.70	27.680	8730.5	331.59	24.852	9325.7
404.24	24.252	7518.4	358.92	27.810	8730.4	340.88	31.365	9320.9
418.14	30.847	7512.6	367.95	33.386	8726.0	349.87	37.607	9316.2
431.75	37.250	7506.9	377.11	38.981	8721.6	358.96	43.864	9311.5
445.69	43.725	7500.9	386.01	44.375	8717.2	368.01	50.019	9306.8
459.37	50.020	7495.1	386.18	44.460	8717.1			
			404.67	55.483	8708.0			

Table 2. Pressure p, amount-of-substance density ρ and temperature T of $\{x_1n\text{-}C_4H_{10} + x_2n\text{-}C_7H_{16} + (1-x_1-x_2)n\text{-}C_{16}H_{34}\}$. Superscript s indicates a saturated condition.

T/K	p/MPa	ρ/mol·m^{-3}	T/K	p/MPa	ρ/ mol·m^{-}	T/K	p/MPa	ρ/mol·m^{-3}
x_1=0.1161, x_2=0.7151			x_1=0.1967, x_2=0.6499			x_1=0.2314, x_2=0.6218		
447.90^s	0.773^s	4942.0^s	418.8^s	0.634^s	5446.0^s	404.40^s	0.557^s	5696.2^s
451.07	1.800	4941.1	423.52	2.500	5444.6	404.74	0.703	5696.1
455.65	3.286	4939.98	427.51	4.127	5443.4	409.35	2.688	5694.7
460.25	4.783	4938.6	432.63	6.061	5441.8	413.90	4.642	5693.3
460.33	4.808	4938.6	441.11	9.472	5439.3	418.50	6.612	5691.8
464.86	6.274	4937.3	441.81	9.639	5439.1	423.11	8.584	5690.4
469.47	7.774	4936.1	450.98	13.208	5436.3	427.78	10.571	5688.9
			460.23	16.781	5433.4	432.41	12.530	5687.4
			469.38	20.297	5430.6	437.06	14.509	5685.9
						441.65	16.452	5684.5
						446.27	18.393	5683.0
						450.75	20.275	5681.6
						450.85	20.314	5681.5
						455.44	22.235	5680.1
						460.10	24.171	5678.6

FIGURE CAPTIONS

Fig. 1. Experimental pressures and temperatures for $\{x_1CO_2 + (1\text{-}x_1)n\text{-}C_7H_{16}\}$ in the single and two-phase regions: ○, $x_1 = 0.2918$; □, $x_1 = 0.3888$; △, $x_1 = 0.4270$.

Fig. 2. Experimental pressures and temperatures for $\{x_1n\text{-}C_4H_{10} + x_2n\text{-}C_7H_{16} + (1\text{-}x_1\text{-}x_2)n\text{-}C_{16}H_{34}\}$ in the single and two-phase regions: ○, $x_1 = 0.1161$, x_2=0.7151; □, $x_1 = 0.1967$, x_2=0.6499; △, $x_1 = 0.2314$, x_2=0.6218.

Fig. 3. Deviations of experimental densities of $\{x_1CO_2 + (1\text{-}x_1)\ n\text{-}C_7H_{16}\}$ from values calculated by using the Peng-Robinson equation of state without volume translation (open symbols) and with volume translation (filled symbols): ○, ●, $x_1 = 0.2918$; □, •, $x_1 = 0.3888$; △, ▲, $x_1 = 0.4270$.

Fig. 4. Deviations of experimental densities of $\{x_1n\text{-}C_4H_{10} + x_2n\text{-}C_7H_{16} + (1\text{-}x_1\text{-}x_2)n\text{-}C_{16}H_{34}\}$ from values calculated by using the unoptimised Peng-Robinson model (filled symbols) and unoptimised one-fluid model (open symbols): ○, ●, $x_1 = 0.1161$, x_2=0.7151; □, •, $x_1 = 0.1967$, x_2=0.6499; △, ▲, $x_1 = 0.2314$, x_2=0.6218.

Fig. 5. Deviations of experimental densities of $\{x_1CO_2 + (1\text{-}x_1)C_7H_{16}\}$ from values calculated by using the one-fluid model: ○, $x_1 = 0.2918$; □, $x_1 = 0.3888$; △, $x_1 = 0.4270$.

Fig. 6. Deviations of experimental densities of $\{x_1n\text{-}C_4H_{10} + x_2n\text{-}C_7H_{16} + (1\text{-}x_1\text{-}x_2)n\text{-}C_{16}H_{34}\}$ from values calculated by using the optimised one-fluid model: ○, $x_1 = 0.1161$, x_2=0.7151; □, $x_1 = 0.1967$, x_2=0.6499; △, $x_1 = 0.2314$, x_2=0.6218.

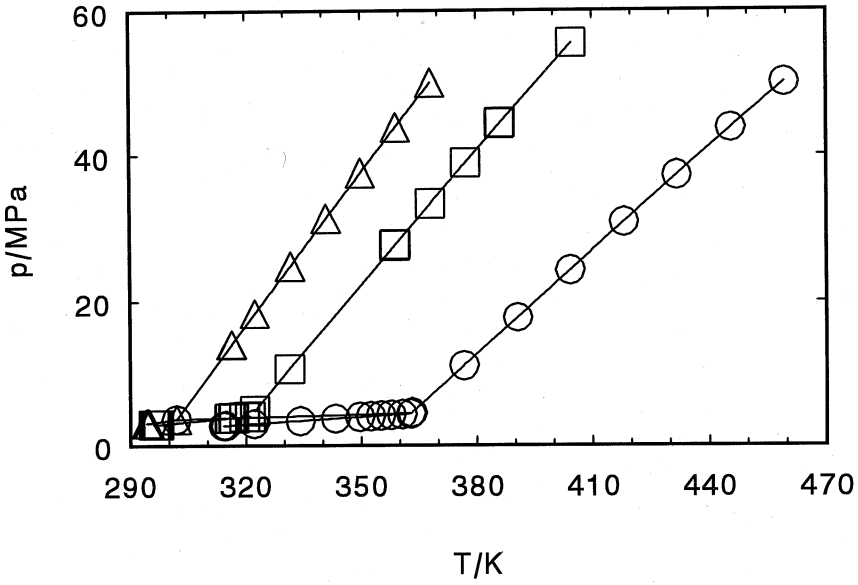
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Fig.1

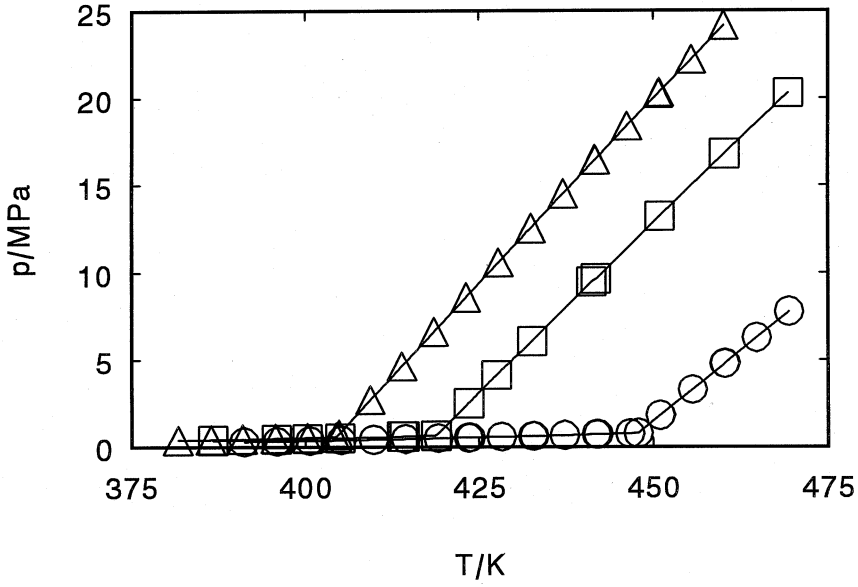
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Fig.2

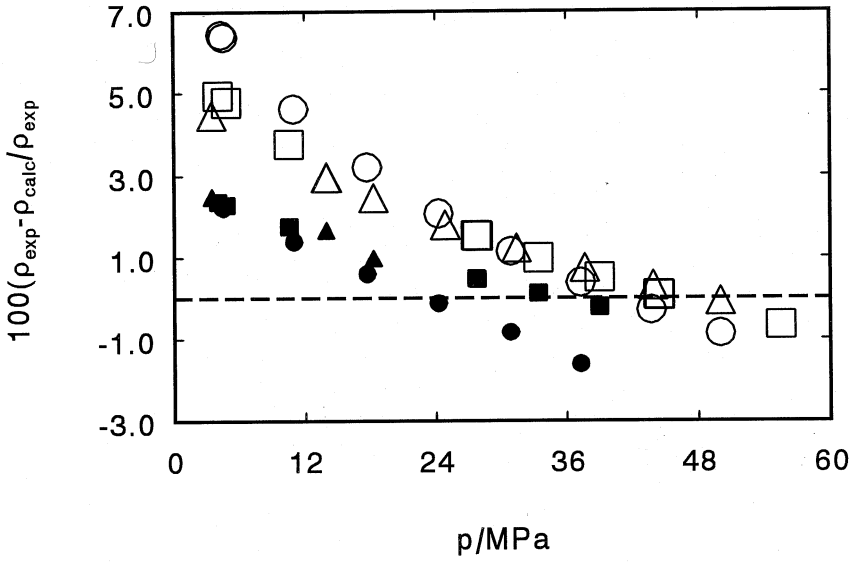
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Fig. 3

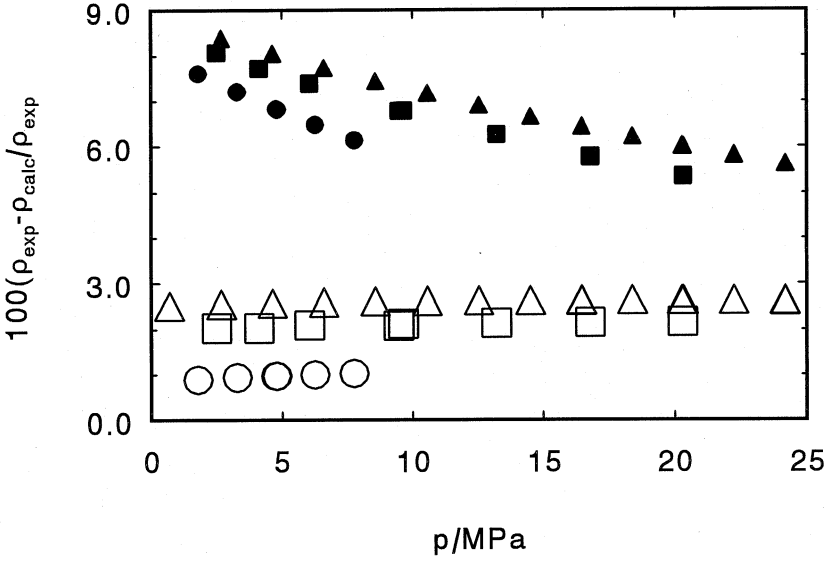
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Fig. 4

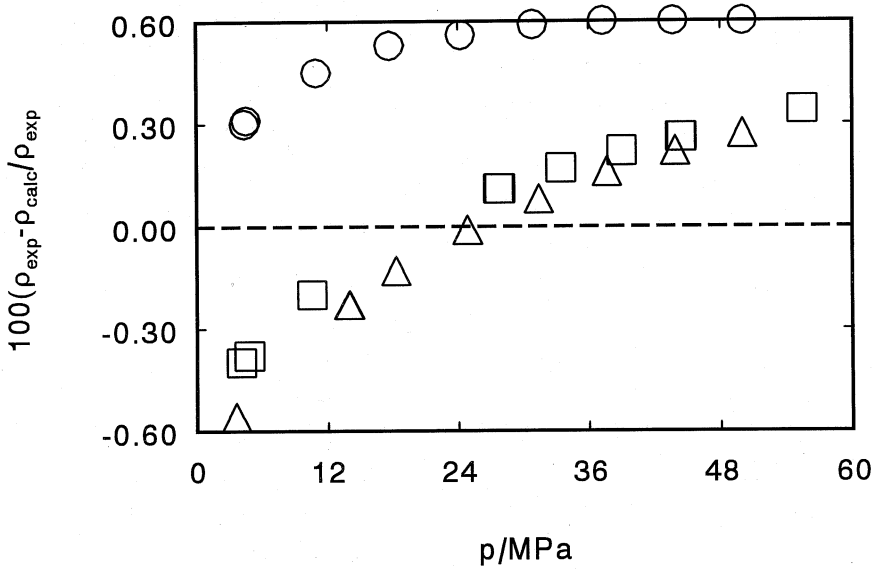
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Fig.5

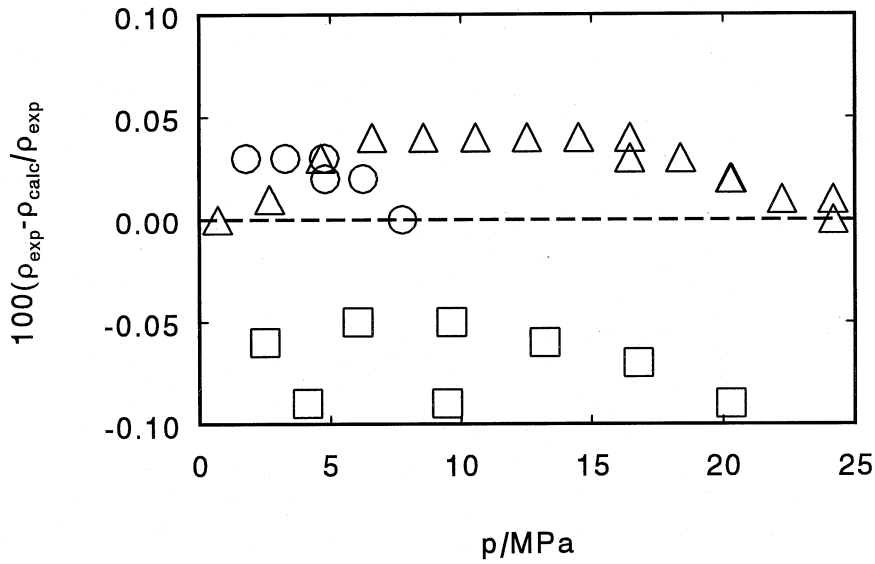
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Fig.6